I. THE STRUCTURE OF VINYL COPOLYMERS
II. THE PREPARATION OF SOME *META*-SUBSTITUTED TRIPHENYLCARBINOLS AND CHLOROMETHANES
SUPPLEMENT
AN ATTEMPTED PREPARATION OF STILBESTROL

BY
THOMAS WILLIAM MASTIN
A.B., Wabash College, 1938
M.S., University of Illinois, 1939

AN ABSTRACT OF A THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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URBANA, ILLINOIS
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I. THE STRUCTURE OF VINYL COPOLYMERS

Introduction

The structures of several vinyl polymers have been determined previous to the present work.[1] In view of the increasingly important place taken by vinyl copolymers throughout the polymer industry, an understanding of their structure is very desirable. In the present investigation an attempt has been made to determine the structure of "Vinylite," the copolymer of vinyl chloride and vinyl acetate.

Experimental and Discussion

Marvel, Sample, and Roy[2] have shown that polyvinylchloride has a head-to-tail structure. The reaction of zinc dust with polyvinylchloride in dilute solution proved to be of primary importance in this determination. Since "Vinylite" contains vinyl chloride units, it seemed possible to gain some knowledge about the structure by use of the zinc treatments. In this connection Wall[3] has calculated the probable number of chlorine atoms which should remain isolated along the polymer chain after complete reaction of zinc with "Vinylite."

A series of commercial and laboratory prepared "Vinylites" ranging from 0.9 to 0.2 mole fraction of vinyl chloride have been treated with zinc dust. The experimental results were compared with the theoretically predicted results. This comparison between theoretical predictions and experimental results indicated a 1,3-structure.

The absence of 1,2-chlorines in "Vinylite" was indicated by failure to react with potassium iodide.

Zinc treated "Vinylite" does not decolorize potassium permanganate but does react with bromine with evolution of hydrogen bromide. These properties would be expected for a cyclopropane ring type of structure which should result from zinc treatments on a "Vinylite" having a 1,3- structure.

II. THE PREPARATION OF SOME *META*-SUBSTITUTED TRIPHENYLCARBINOLS AND CHLOROMETHANES

Introduction

Hexaphenylethane was found to dissociate to triphenylmethyl radicals by Gomberg[4] in 1900. The effect of various substituents in the rings of hexaphenylethane has been studied in this laboratory.[5] The present work describes the preparation of some *meta*-substituted triphenylcarbinols and chloromethanes as intermediates in the synthesis of the corresponding hexaarylethanes.

Experimental and Discussion

The triarylcarbinols were synthesized by adding Grignard reagents to esters. By this procedure the following carbinols were prepared. (a) di-*m*-cyclohexylphenyl-*p*-cyclohexylphenylcarbinol, (b) di-*p*-cyclohexylphenyl-*m*-cyclohexylphenylcarbinol, (c) di-*m*-cyclohexylphenyl-*p*-*tert*-butylphenylcarbinol, (d) di-*p*-*tert*-butylphenyl-*m*-cyclohexylphenylcarbinol, and (e) di-*m*-*tert*-butylphenyl-*p*-cyclohexylphenolcarbinol.

Only carbinol (a) was isolated as a crystalline compound but the corresponding chloromethanes for all except (d) were prepared and characterized.

Hexaarylethanes were obtained from carbinols (a), (b), and (c), and their dissociation reported as 41 ± 8 percent, 20 per cent, and approximately 15 per cent, respectively.

SUPPLEMENT
AN ATTEMPTED PREPARATION OF STILBESTROL

Since Dodds and co-workers[6] discovered that p,p′-dihydroxy-α,β-diethylstilbene had pronounced estrogenic activity, various methods have been used and others tried for the synthesis of this compound. The present work describes another attempted approach to the problem.

3,4-Dihydroxy-3,4-di-(*p*-hydroxyphenyl) hexane has been prepared in low yields by electrolytic reduction in alkaline

solution of *p*-propiophenol. Attempts to convert this pinacol to stilbestrol by treatment with phosphorus and iodine, and with hydrogen iodide were unsuccessful.

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VITA

The writer was born in New Castle, Indiana December 19, 1913. He attended secondary schools there and was graduated from New Castle High School in 1932. He studied at Wabash College from September 1933 to June 1938, receiving a Bachelor of Arts degree in 1938. In the fall of 1938 he entered the Graduate School of the University of Illinois and held a research assistantship in chemistry for the year 1938-39. He received a Master of Science degree in 1939 and continued his studies until August 1940 at which time he left for a year to work in the chemical industry at Detroit, Michigan. He took up his graduate studies in chemistry again at the University of Illinois in September 1941. For the year 1941-42 he held a research appointment in the Physics Department.

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